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(54) Title: HEAT STABILIZED, FLAME RETARDANT THERMOPLASTIC POLYMER COMPOSITIONS**(57) Abstract**

Heat stabilized, flame retardant polymer compositions include a halogen based flame retardant such as hexabromocyclododecane, zeolite A heat stabilizer, and a transition metal compound such as a zinc stearate lubricant. The compositions are stable at high temperatures even when subjected to multiple heating processes and also have unique polymer foam forming properties when compared with compositions containing a different heat stabilizer.

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**HEAT STABILIZED, FLAME RETARDANT
THERMOPLASTIC POLYMER COMPOSITIONS**

This invention relates generally to heat stabilized, flame retardant thermoplastic polymer compositions and more particularly to thermoplastic polymer compositions which include halogen-based flame retardants, such as cycloaliphatic bromine compounds, zeolite A heat stabilizers and transition metal compounds such as zinc stearate.

- 5 Halogen-containing materials, for example, cycloaliphatic organic compounds such as hexabromocyclododecane (HBCD) are widely used in thermoplastic polymer compositions to impart flame retardant properties to the compositions. However, their presence in the thermoplastic polymer-based compositions has the drawback of lowering thermal stability. This can cause serious color and/or viscosity problems when the compositions are exposed to high processing temperatures.
- 10 In order to improve their thermal stability, it is customary to add a stabilizing agent, such as hydrotalcite, tetrasodium pyrophosphate or dibutyl tin maleate. However, when these stabilized compositions are subjected to multiple heating processes, such as in attempting to re-use polymer scrap or when forming masterbatches which are reheated during their incorporation into the bulk of the heat-softened thermoplastic polymers, deterioration of the halogen-based flame retardants, as
- 15 well as the polymer itself can occur. This is evidenced by discoloration of the compositions. Heat deterioration is especially a problem when the polymer compositions contain even very small portions of transition metal compounds such as zinc stearate, which is a preferred lubricant for many extrusion and molding applications. Using lower processing temperatures may help, but this extends processing times and lowers throughput.
- 20 It has now been found that when zeolite A is added to thermoplastic polymer compositions which contain transition metal compounds and halogenated aliphatic compounds, they are heat stable even when subjected to multiple heatings. It has also been found that when forming polymer foams from such compositions, the zeolite A does not increase foam density to the extent that occurs when using other heat stabilizers.
- 25 In accordance with this invention, there is provided a heat stabilized, flame retardant polymer formulation which comprises a thermoplastic polymer, a transition metal compound, a flame retardant amount of a halogen-based flame retardant, and a heat stabilizing amount of zeolite A.

Also provided is a masterbatch composition which comprises from 10 to 90 weight percent thermoplastic polymer and from 10 to 90 weight percent of additives which include at least a halogen-based flame retardant, zeolite A, and a transition metal compound.

5 Additionally provided is a process for manufacturing a flame retardant article from a thermoplastic polymer composition comprising the steps of (i) heating and mixing a first thermoplastic polymer composition, said composition containing a transition metal compound and having been formed by combining a heat-plastified thermoplastic polymer with a halogen-based flame retardant, and zeolite A, with a second thermoplastic polymer composition to form a heat-plastified polymer gel composition, (ii) either expressing the heat-plastified thermoplastic polymer
10 gel composition from a die or injecting said gel composition into a mold so as to form a flame retardant article, and (iii) cooling the article to a temperature at which the article is self-supporting.

The thermoplastic polymers and copolymers for use in the invention include those organic polymers which are usually associated with flammability problems when formed into a broad range of plastic articles, both in the form of solid objects and foams. Non-limiting examples of such
15 polymers include polyolefins, polyesters, polyamides, polycarbonates, styrenic polymers, and polyurethanes. Specific examples of such polymers include high and low density polyethylene, polypropylene, polystyrene, ethylene-propylene and ethylene-propylene-diene copolymers, nylon 6 and polyethyleneterephthalate. The invention is particularly useful with styrenic polymers.

Styrenic polymers are usually classified as general-purpose polystyrene (GPPS) or as impact
20 modified polystyrene (IPS). GPPS is a high molecular weight, clear polymer which is hard, rigid and free of odor and taste. It finds use in producing moldings and extrusions including foams and films. IPS is a rubber-modified polystyrene which is characterized by its toughness and resistance to abuse. The rubber is dispersed in the polystyrene matrix in the form of discrete particles. IPS is not clear, but rather is either translucent or opaque depending upon the amount of rubber used. The
25 art recognizes two types of IPS, i.e., medium-impact polystyrene (MIPS) and high-impact polystyrene (HIPS), the former containing less rubber than the latter. HIPS can be generally characterized as having an 8 to 18 wt% rubber content. In some instances, mixtures of IPS and GPPS are used to achieve certain blends of properties.

For the purposes of this invention, the styrenic polymer can be GPPS, IPS or a mixture of the
30 two. GPPS is generally used in making foams but GPPS-IPS mixtures are sometimes used. The GPPS and IPS may be homopolymers, copolymers or block polymers and are formed from such vinyl aromatic monomers as styrene, ring-substituted methyl or polymethylstyrenes, ring-substituted

ethyl or polyethylstyrenes, ring-substituted propyl or polypropylstyrenes, ring-substituted butyl or polybutyl styrenes, ring-substituted mixed polyalkylstyrenes wherein the alkyl groups differ from each other, alpha-methylstyrene, ring-substituted methyl- or polymethyl-alpha-methylstyrenes, propyl- or polypropyl-alpha-methyl-styrenes, butyl- or polybutyl-alpha-methylstyrenes, ring-substituted mixed polyalkyl-alpha-methylstyrenes wherein the alkyl groups differ from each other, ring-substituted alkyl- or polyalkylchlorostyrenes in which the alkyl group(s) contain(s) from one to four carbon atoms, and similar polymerizable styrenic monomers--i.e., styrenic compounds capable of being polymerized by means of peroxide or like catalysts into thermoplastic resins. Homopolymers and copolymers of simple styrenic monomers (e.g., styrene, p-methyl-styrene, 2,4-dimethylstyrene, alpha-methylstyrene, and p-chloro-styrene) are preferred from the standpoints of cost and availability.

The IPS may be either medium impact polystyrene (MIPS) or high-impact polystyrene (HIPS). The rubber used in effecting impact modification is most often a butadiene rubber.

The halogen-based flame retardants used in this invention may be any such flame retardants that are commonly used in this field and which are subject to heat stability problems, such as aliphatic, cycloaliphatic, and mixed aliphatic-aromatic organic halogen compounds in which the aliphatic groups contain halogen. Examples that may be cited include tetrabromoethane, tetrabromobutane, hexabromocyclododecane, acetylene tetrabromide, pentabromochlorocyclohexane, ethylene bis(dibromobornane dicarboximide) (BN 451), dibromoethyldibromocyclohexane (BCL 462), tetrabromocyclooctane (BC-48), melamine hydrobromide, tris(2,3-dibromopropyl)isocyanurate, tetrabromobisphenol A bis(2,3-dibromopropyl ether), 2,3-dibromopropylpentabromophenyl ether, tetrabromophthalic anhydride and esters thereof including RB-79 and PHT-4 diol, chlorinated polyethylenes, chlorinated paraffins, chlorendic anhydride and derivatives thereof. There is no particular limit on the amount in which these halogen-based flame retardants are added, it being suitable to vary the amount as appropriate according to the desired degree of flame retardation. It is generally preferable to use 1 - 35 parts by weight, per 100 parts by weight of thermoplastic polymer, of one of these flame retardants alone or of two or more together. The invention is particularly effective with cycloaliphatic flame retardants which are less heat stable, especially in the presence of Lewis acids. A preferred flame retardant is a hexabromocyclododecane material. This material is a mixture of isomers.

Both the low-melt and high-melt hexabromocyclododecane products having individual melting point ranges within the general range of 170° C - 200° C can be used. A most highly

preferred product is HBCD-LM flame retardant available from Albemarle Corporation. This HBCD material has a melting point range of 178° C - 188° C and a minimum melt point of 175° C.

5 The amount of flame retardant used is that amount which will render the formulation flame retardant. For the purposes of this invention, the term "flame retardant" is to mean that the non-foamed formulations, when tested in accordance with UL 94, obtains a rating of at least V-2. The UL 94 test is an Underwriters Laboratories Inc. test entitled "Test for Flammability of Plastic Materials for Parts in Devices and Appliances" and for foam materials when tested in a Steiner Tunnel in accordance with UL 723 and ASTM E-84, obtains a Standard Building Code rating of at least C (flame spread index 76 - 200, smoke density ≥ 450) and, preferably, a rating of A or B (A = 10 flame spread index of 0 - 25, B = flame spread index of 26 - 75). For cycloaliphatic halogen-based flame retardants such as HBCD, from 0.5 to 8 wt% is generally used, based on the total weight of formulation in order to obtain such ratings. Usually, highest ratings can be obtained in foams using from 1.0 wt% HBCD at a foam thickness of 1.27 cm (0.5") up to 3.0 wt% at a foam thickness of 5.08 cm (2.0").

15 The zeolite A used in the practice of this invention can be represented by the generalized formula for zeolite, $M_{2n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$, wherein M is a group IA or IIA element, such as sodium, potassium, magnesium and calcium. For a sodium zeolite, the formula is $Na_2 \cdot OAl_2O_3 \cdot xSiO_2 \cdot yH_2O$. The value of x normally falls within the range of 1.85 ± 0.5 . The value for y can also be variant and can be any value up to 6. On average, the value of y will be 5.1. For 20 a sodium zeolite A the formula can be written as $1.0 \pm 0.2Na_2O \cdot AlO_3 \cdot 1.85 \pm 0.5SiO_2 \cdot yH_2O$, wherein the value of y can be up to 6. An ideal zeolite A has the following formula, $(NaAlSiO_4)_{12} \cdot 27H_2O$. Zeolite A is commercially available and can be purchased from Albemarle Corporation under the trademark EZA. The zeolite A is not modified by reaction with compounds such as inorganic halides.

25 The amount of zeolite A used is that amount which effects thermal stabilization of the formulation. Generally, for most formulations of the invention, the amount of zeolite A used will be within the range of from 0.1 to 5 wt% based upon the total weight of the formulation. A preferred amount is within the range of from 0.6 to 1.5 wt%.

30 Transition metal containing compounds, for example, lubricants, nucleating agents, dyes, or pigments are commonly present in the thermoplastic polymer compositions in amounts of from 0.005 to 1.0 weight percent or more of the compositions. Non-limiting examples of these compounds include lubricants such as zinc stearate and other Zn, Cu, and Fe, salts of fatty acids such as stearic,

tallow, and coco fatty acids and the dimer of oleic acid. Aryl carboxylate and sulfonate salts, i.e., benzoate or terephthalate salts, are used as nucleators. It has been found that the transition metal compounds have a destabilizing effect as they tend to cause serious degradation problems, especially with cycloaliphatic flame retardant containing polymer compositions, upon the achievement of high temperatures and/or undergoing a heat history (masterbatch heat experience + processing heat experience or other multiple heating processes such as scrap recycle). This can occur not only when the transition metal compound is present in functional (i.e., lubricating, nucleating, or colorant) amounts of 100 to 1,000 ppm or more of transition metal by weight of the polymer formulation, but even when the transition metal is only incidentally present in amounts of less than 100 ppm (as small as 10 ppm) by weight of the polymer formulation as a result, for example, of incorporating polymer scrap into the composition. The presence of the zeolite A stabilizer renders the compositions exceptionally heat stable when they are subjected to such multiple heatings.

In addition to the thermoplastic polymer, halogen-based flame retardant, transition metal compound, and zeolite A, there can be present in the formulation other conventional additives in their conventional amounts. Exemplary of such additives are: fillers, pigments, dyes, impact modifiers, UV stabilizers, antioxidants, processing aids, nucleating agents, and lubricants.

All of the constituents are blended in any conventional manner and can be blended in any order. For example, the constituents can first be dry mixed and then fed to a Banbury or Herschell mixer or to a twin screw extruder such as a ZSK 30 Werner and Pfleiderer extruder, to obtain a blended material for feed, for example, to an injection molding apparatus, such as a 500 kN Demag machine. Blending temperatures will generally be within the range of from 180 to 200° C and injection molding temperatures will generally be in the range of 180 to 250° C.

A convenient way to add the flame retardant and stabilizer to the thermoplastic polymer is as a masterbatch which is a concentrated, heat blended or extruded mixture of the various additives in the polymer. The concentration of additives usually ranges from 10 to 90 percent by weight of the total weight of masterbatch composition, with the balance of 10 to 90 weight percent being polymer. The masterbatch is then added to the bulk of the thermoplastic polymer material, which may already contain other additives such as a zinc stearate lubricant. The masterbatch is added in proportions to give the desired concentration of additives in the final blended product and usually in proportions of from 1 to 50 percent by weight of total weight of the final blended polymer composition.

In one embodiment of the article manufacturing process of the invention, thermoplastic polymer foam materials, for example, rods or rectangular boards, are formed, as is known, by mixing the additives, either individually or as a masterbatch, with the polymer, preferably a styrenic polymer, and then feeding the mixture to an extruder along with a foaming agent and, optionally, a nucleating agent, such as commercially available carbonate based materials, for example, the material sold under the trademark, Safoam - FP.

Any of a wide variety of known foaming agents or blowing agents can be used in producing the expanded or foamed flame resistant polymers. U.S. Patent No. 3,960,792 gives a listing of some suitable materials. Generally speaking, volatile carbon-containing chemical substances are the most widely used for this purpose. They include, for example, such materials as aliphatic hydrocarbons including ethane, ethylene, propane, propylene, butane, butylene, isobutane, pentane, neopentane, isopentane, hexane, heptane and mixtures thereof; volatile halocarbons and/or halohydrocarbons, such as methyl chloride, chlorofluoromethane, bromochlorodifluoromethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, dichlorofluoromethane, dichlorodifluoromethane, chlorotrifluoromethane, trichlorofluoromethane, sym-tetrachlorodifluoroethane, 1,2,2-trichloro-1,1,2-trifluoroethane, symdichlorotetrafluoroethane; volatile tetraalkylsilanes, such as tetramethylsilane, ethyltrimethylsilane, isopropyltrimethylsilane, and n-propyltrimethylsilane; and mixtures of such material. One preferred fluorine-containing blowing agent is 1,1-difluoroethane also known as HFC-152a (FORMACEL Z-2, E.I. duPont de Nemours and Co.) because of its reported desirable ecological properties. Water-containing vegetable matter such as finely-divided corn cob can also be used as blowing agents. As described in U.S. Patent No. 4,559,367, such vegetable matter can also serve as fillers. Use of carbon dioxide as a foaming agent, or at least a component of the blowing agent, is particularly preferred because of its innocuous nature vis-à-vis the environment and its low cost. Methods of using carbon dioxide as a blowing agent are described, for example, in U.S. Patent No. 5,006,566 wherein the blowing agent is 80 to 100% by weight of carbon dioxide and from 0 to 20% by weight of one or more halohydrocarbons or hydrocarbons that are gaseous at room temperature, in U.S. Patents Nos. 5,189,071 and 5,189,072 wherein a preferred blowing agent is carbon dioxide and 1-chloro-1,1-difluoroethane in weight ratios of 5/95 to 50/50, and in U.S. Patent No. 5,380,767 wherein preferred blowing agents comprise combinations of water and carbon dioxide. Such materials can be utilized with appropriate flame retarded thermoplastic polymer compositions of this invention.

The invention is further illustrated by, but is not intended to be limited to, the following examples.

Masterbatch Formation

Example 1

5 A masterbatch of polystyrene (Styron® 685D GPPS, Dow Chemical Co.), which polystyrene contained 136 ppm by weight of zinc as zinc stearate lubricant, was formed by blending, at a temperature of 150° C - 180° C, with mechanical mixing (100 rpm) in a Werner and Pfleiderer ZSK 30 twin-screw, co-rotating extruder, 77 parts by weight of polystyrene with 23 parts by weight of a mixture containing 75 wt% HBCD-LM flame retardant and 25 wt% zeolite A. The polymer and
10 flame retardant were gravimetrically fed from two separate feeders. Barrel zone temperatures were 150 - 160 - 170 - 175, and 180° C and the throughput was 6 Kg/hour. The extruded strand was pelletized in line.

Comparative Example

15 A masterbatch was prepared using the same zinc containing polystyrene and flame retardant, but with dibutyl tin maleate and 2,2'-oxamidobisethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (Naugard XL-1) as the stabilizers. The proportions were 76 wt% polystyrene and 24 wt% of a mixture containing 94 wt% HBCD-LM, 4 wt% dibutyl maleate, and 2 wt% Naugard XL-1 stabilizer. When an attempt was made to form a masterbatch which contained only the styrenic polymer composition and HBCD with no stabilizer, it turned black and degraded and no useful product was
20 obtained. When a zinc free (< 1 ppm) polystyrene was used with HBCD, an amber colored masterbatch product could be obtained.

Example 2-5

A 3.175 cm (1.25 inch) segmented single screw extruder having a 40/1 length to diameter ratio and a rod die was used for foaming several mixtures of the masterbatch prepared in Example
25 1 with the same type of GPPS polystyrene used to make the masterbatch. The screw was designed to operate in three stages: a plasticization section, a gas injection section, and a metering and mixing section. Several samples were prepared to provide different concentrations of additives in the polymer. A small amount (0.05 wt% of composition) of Safoam - FP nucleating agent was also dry blended with the mixture. The mixtures were metered through a single screw feeder. CO₂ gas was
30 used as a physical blowing agent for foaming the polystyrene blends. A description of the samples is given in Table 1 and the melt temperatures and CO₂ gas injection pressures are given in Table 2. The density of the foam products was also measured by the water displacement technique on samples.

of the product and the results are reported in Table 1. The lowest density product was obtained at a gas injection pressure of 5515 - 5654 kPa (800 - 820 psi), a melt temperature of 143° C - 149° C (290° F - 300° F) and at melt pressures above 9653 pKa (1400 psi). Temperatures at the different barrel zones were typically, in degrees C, 38 - 149 - 177 - 177 - 166 - 149 - 149 - 149 - 149 - 143 -
 5 and 141 - 144 (melt) (in degrees F, 100 - 300 - 350 - 350 - 330 - 300 - 300 - 300 - 300 - 290 and 286 - 292). As a comparison, several samples of foam were made in the same way but using the masterbatch composition from the first Comparative Example which contained a tin maleate and Naugard XL-1 stabilizers.

10 It was observed that the comparison samples appeared dark when extruded at a high temperature, e.g., 204° C (400° F). The use of a lower processing temperature was needed to reduce the color formation. In contrast, the foam samples prepared from the composition of the invention had much less color, even at high processing temperatures. It appears then, that even though the tin maleate and Naugard XL-1 stabilizers were adequate to reduce decomposition during masterbatch formation, significant decomposition occurred as a result of the second heating step when the
 15 masterbatch was used in the foaming process. The compositions of the invention were stable during the second heating step even at high processing temperatures, despite the presence of the zinc stearate lubricant which otherwise would accelerate the decomposition of the bromine containing styrenic polymer composition.

TABLE 1

20	<u>Example</u>	<u>Wt%</u>	<u>Wt% Br</u>	<u>Fresh Foam</u>	<u>Aged Foam</u>
		<u>HBCD-Zeolite</u>	<u>Theory</u>	<u>Density g/cc</u>	<u>Density g/cc*</u>
	Control	0.00	0.00	0.10	0.072
	2A	0.50	0.28	0.10	0.083
	2B	0.50	0.28	0.10	0.075
	3	0.70	0.38	0.11	0.075
25	4	2.00	1.12	0.11	0.078

<u>Comparison</u>	<u>Wt%</u> <u>HBCD-Tin Maleate-</u> <u>Naugard XL-1</u>
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1	0.50	0.35	0.10	0.072
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2	1.50	1.05	0.12	0.076
3	2.00	1.40	0.14	0.090

*Measurements made 8 to 10 weeks after manufacture of the samples.

TABLE 2

5	<u>Example</u>	<u>Melt Temp (° C)</u>	<u>CO₂ Injection Pressure (kPa)</u>
	Control	141 (286° F)	5606 (813 psi)
	2A	142 (288° F)	5661 (821 psi)
	2B	143 (290 ° F)	5544 (804 psi)
	3	144 (292° F)	5654 (820 psi)
10	4	142 (289° F)	5675 (823 psi)
	<u>Comparison</u>		
	1	143 (290° F)	5626 (816 psi)
	2	141 (287° F)	5606 (813 psi)
	3	141 (286° F)	5681 (824 psi)

15 As illustrated by the foam density data in Table 1, in addition to being more heat stable than the comparative materials, the combination of additives used in Example 4, at the higher bromine level required to obtain adequate flame retardancy, such as when forming 5 to 7.6 cm (2 to 3 inch) thick building insulation panels, also had less effect on the foam density. A significant increase in foam density was observed at a bromine level of 1.4% in Comparison 3 when using the tin maleate and Naugard XL-1 stabilizers. In contrast, the foam density of the samples made according to the invention remained about the same (within 10 - 15%) with increasing bromine levels besides having improved color and thermal stability in the presence of the zinc.

Example 6

25 Six general purpose polystyrene formulations (GPPS) were compounded in a Haake twin-screw extruder at 60 rpm by bag-mixing 3 weight percent of different mixtures of flame retardants and zeolite A with 97 weight percent of GPPS and feeding the mixture from a single hopper into the extruder. The temperature profile was 190 - 220 - 240 - 252° C. The extruded strand was pelletized

in line. The pelletized composition was then injection molded into disks using a Battenfeld BSKM 100/40 injection molding machine under the following process conditions:

- holding time = 10 seconds
- cooling time = 15 seconds
- 5 mold open time = 2 seconds
- temperature profile = 199 - 221 - 227° C
- nozzle = 75%
- mold temperature = 45° C
- injection pressure = 8964 kPa (1300 psi) on ram
- 10 holding pressure = 4827 kPa (700 psi) on ram

The color of the injection molded disks was measured using a HunterLab scale, D65 illuminant, 10° observer, and integrated-sphere geometry. The Melt Flow Index (ASTM D1238) procedure A, was measured at 200° C/5 Kg. The formulations and results are given in Table 3.

TABLE 3

15	<u>Ingredients</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>6A</u>	<u>D</u>	<u>6B</u>
	GPPS	97	97	97	97	97	97
	For Mix 1	3	3				
	For Mix 2			3	3		
	For Mix 3					3	3
20	Zn as Zn Stearate	0	50ppm	0	50ppm	0	50ppm

Color Test

Initial Color

	L	67.5	---	68.7	65.6	69.4	72.3
	a	5.8	---	-0.5	0.7	-0.8	-0.4
25	b	23.4	---	7.2	11.2	8	10.8

Melt Flow

(g/min)	12.4	NM	10.8	10.2	10	10.3
200° C / 5kg						

Mix 1 = 94% HBCD, 4% dibutyl tin maleate, 2 % Naugard XL-1 stabilizer

Mix 2 = 75% HBCD, 25% zeolite A

Mix 3 = 75% HBCD, 20% zeolite A, 2% dibutyl tin maleate, 1% Naugard XL-1 stabilizer,
2% Ethanox 330 antioxidant

5 * = sample was very dark after extrusion and was not injection molded

NM = not measured.

The results given in Table 3 show that, after extrusion and molding, the zeolite A containing compositions of the invention (Formulations 6A and 6B) had about the same stability as Formulations C and D which did not contain the zinc stearate. In contrast, the tin maleate stabilized

10 Formulation B had such poor stability in the presence of the zinc stearate that it turned very dark after the initial extrusion. Such a flame retardant zinc containing polymer material would not be useful in forming molded objects.

CLAIMS

1. A formulation comprising a thermoplastic polymer, a transition metal compound, a flame retardant amount of a halogen-based flame retardant and a heat stabilizing amount of zeolite A.
- 5 2. The formulation according to claim 1 wherein said halogen-based flame retardant is a cycloaliphatic organic halogen compound.
3. The formulation according to claim 2 wherein said organic halogen compound is HBCD and said transition metal compound is a transition metal salt of a fatty acid.
4. The formulation according to claim 1 wherein said halogen-based flame retardant is
10 present in an amount of from 1 to 35 parts by weight per 100 parts by weight of formulation, said zeolite A is present in an amount of from 0.1 to 5 parts by weight per 100 parts by weight of formulation and said transition metal compound is present in an amount of from 0.005 to 1.0 parts by weight per 100 parts by weight formulation.
5. The formulation according to claim 1 wherein said thermoplastic polymer is a styrenic
15 polymer.
6. The formulation according to claim 4 wherein the transition metal is present in an amount of from 10 to 1,000 ppm by weight of formulation.
7. The formulation according to claim 6 wherein said transition metal is zinc.
8. A masterbatch composition which comprises from 10 to 90 weight percent
20 thermoplastic polymer and from 10 to 90 weight percent of additives which include at least a halogen-based flame retardant, zeolite A, and a transition metal compound.
9. The composition according to claim 8 wherein said halogen-based flame retardant is a cycloaliphatic halogen compound.
10. The composition according to claim 9 wherein said flame retardant is HBCD.
- 25 11. The composition according to claim 8 wherein said transition metal compound is a transition metal salt of a fatty acid.
12. The composition according to claim 11 wherein said transition metal is zinc.
13. The composition according to claim 8 wherein said transition metal is present in an amount of from 10 to 1,000 ppm by weight of said composition.

14. The composition according to claim 13 wherein said thermoplastic polymer is a styrenic polymer, said halogen-based flame retardant is a cycloaliphatic bromine compound and said transition metal compound is a transition metal salt of a fatty acid.

5 15. The composition according to claim 14 wherein said bromine compound is HBCD and said transition metal compound is zinc stearate.

10 16. A process for manufacturing a flame retardant article from a thermoplastic polymer composition comprising the steps of (i) heating and mixing a first thermoplastic polymer composition, said composition containing a transition metal compound and having been formed by combining a heat-plastified thermoplastic polymer with a halogen-based flame retardant, and zeolite A, with a second thermoplastic polymer composition to form a heat-plastified polymer gel composition, (ii) either expressing the heat-plastified thermoplastic polymer gel composition from a die or injecting said gel composition into a mold so as to form a flame retardant article, and (iii) cooling the article to a temperature at which the article is self-supporting.

15 17. The process according to claim 16 wherein said first and second thermoplastic compositions comprise styrenic polymer, said halogen-based flame retardant is a cycloaliphatic bromine compound and said transition metal compound is a fatty acid salt.

18. The process according to claim 17 wherein said first thermoplastic polymer composition is a masterbatch.

20 19. The process according to claim 17 wherein said first thermoplastic polymer composition is polymer scrap or recycled polymer.

20. The process according to claim 17 wherein said flame retardant is HBCD and said transition metal compound is zinc stearate.

25 21. An improved flame retardant polymer composition which includes a thermoplastic polymer, a halogen-based flame retardant and a transition metal compound, the improvement comprising including zeolite A in said composition so as to provide said composition with improved color and heat stability in the presence of the transition metal.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/16056

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K13/02 C08L25/02 C08J3/22 //(C08K13/02, 3:34, 5:02, 5:098)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 427 173 A (ENIMONT) 15 May 1991 see page 2, line 50 - page 3, line 6; claims 1,3,7,16,17 ---	1-3,7
X	DATABASE WPI Section Ch, Week 8722 Derwent Publications Ltd., London, GB; Class A12, AN 87-150916 XP002048115 & DD 242 618 A (VEB GUMMIW THURINGE) , 4 February 1987 see abstract ---	1-3
A	EP 0 410 538 A (DOW) 30 January 1991 see claims 1,3,7,11,17 --- -/-	1,5,7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

25 November 1997

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 732 359 A (BASF) 18 September 1996</p> <p>see claim 1; example 13</p> <p>-----</p>	<p>1, 5, 11,</p> <p>12</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/16056

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